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Laser-Induced Breakdown Spectroscopy Continuous Emissions Monitor for Metals

Characterization, Monitoring, and Sensor Technology
Crosscutting Program

Prepared for
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Office of Science and Technology

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INNOVATIVE TECHNOLOGY
Summary Report

Laser-Induced Breakdown Spectroscopy Continuous Emissions Monitor for Metals

Tech ID 18

Characterization, Monitoring, and Sensor Technology
Crosscutting Program

Demonstrated at
Clemson University Vitrification Test Facility, Clemson, North Carolina
Plasma Hearth Facility at the SAIC STAR Center, Idaho Falls, Idaho
U.S. EPA Incineration Research Facility, Jefferson, Arkansas
Balboa Pacific Corporation, Santa Fe Springs, California
TSCA Incinerator, K-25 Site, Oak Ridge, Tennessee
U.S. EPA Rotary Kiln Incinerator Simulator, Research Triangle Park, North Carolina
Contained Burn Facility at Naval Air Weapons Station, China Lake, California
ICI Explosives Environmental, Inc. Incineration Facility, Joplin, Missouri

INNOVATIVE TECHNOLOGY
Summary Report

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at www.em.doe.gov/ost under "Publications."

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SECTION 1
SUMMARY

The U.S. Department of Energy (DOE) sponsored a technology development and field demonstration program focused on a continuous emissions monitor (CEM) capable of providing real-time measurements of metal emissions in the waste streams of thermal treatment facilities. This project was initiated in 1993 at Sandia National Laboratories, Livermore, California, and lead to the development of a prototype CEM based on an optical emission technique referred to as Laser-Induced Breakdown Spectroscopy (LIBS).

Technology Summary

- Technology Needs and Technology Drivers

Thermal treatment, notably incineration, has been a primary means for the processing of toxic and low-level radiological waste (i.e. mixed waste) in the DOE complex. Alternative processes to incineration, such as plasma hearth processing and vitrification, are candidate technologies for waste treatment, but to date such processes have been limited to pilot-scale operations. Incineration has also been adopted by the Department of Defense (DoD), including facilities dedicated to munitions destruction. In the private sector, thermal treatment is widely used to treat waste streams, including systems dedicated to on-site process streams and commercial facilities that accept waste from outside sources.

While modern incineration processes enjoy significant support from the engineering and scientific communities as a sound means of waste treatment, local civic and environmental groups have at times been outspoken critics of such facilities. Regulatory agencies, including federal, state and local agencies, must address community concerns by permitting facilities based on the best available science and risk assessment. While cooperation among all parties is at times achieved, the single issue of smokestack emissions levels often remains a divisive one. To this end, community groups, regulators, and facility operators are generally in agreement on the need for accurate emissions data. Accordingly, the development of accurate, real-time continuous emissions monitors (CEMs) has been the focus of significant program efforts. A reliable and accurate CEM system can facilitate regulatory compliance, provide assurances to neighboring communities as to the reliability and efficacy of treatment facilities, and provide facility operators with feedback for improved system optimization and efficiency leading to increased cost effectiveness.

- *Overview of Technology*

The prototype CEM is based on an optical emission technique referred to as laser-induced breakdown spectroscopy (LIBS). The developed LIBS system uses a high peak power pulsed laser beam to form a small spark (i.e. breakdown) directly in the effluent waste stream. The gas sample within this laser-induced spark (which is less than 1 mm in diameter) is converted to a plasma state, with temperatures approaching 25,000 K (45,000^{0}F). All molecules and small particles are dissociated into single atoms within the energetic plasma, and the electrons within these atoms subsequently gain energy, moving from their ground electronic state into excited electronic states. The electrons relax back to the ground state by emitting light at characteristic wavelengths in a process known as atomic emission. Each element is characterized by unique atomic emission lines, which like fingerprints enable the identification of constituent elements within the plasma. Furthermore, the intensity of the atomic emission lines can be used to quantify elemental concentrations. The current CEM system eliminates sample transport issues by firing the laser beam directly into the process exhaust stream to create the laser-induced plasma. The emitted light from the plasma is collected and processed in real-time using a spectrometer and detector system controlled by a single PC or laptop computer. The system is targeted for the detection of toxic metals, primarily the Resource Conservation and Recovery Act (RCRA) metals arsenic, beryllium, cadmium, chromium, lead and mercury, although other Clean Air Act metals are accessible. The technology has been incorporated into a compact and robust field-deployable package, and has been tested at a number of treatment facilities, as described in this document.

- *Potential Technology End-users*

The primary need for the LIBS-based CEM system is for monitoring of effluent stacks from DOE waste treatment facilities in support of development, demonstration, and facility permitting of alternatives to incineration. The Toxic Substance Control Act (TSCA) Incinerator at the K-25 site at Oak Ridge, Tennessee, also remains committed to the treatment of DOE mixed waste and fully supports the testing, evaluation, and deployment of CEM technologies, including the recent deployments particulate matter (PM) and mercury (Hg) CEM systems. Non-DOE applications include DoD munitions deactivation furnaces and contained burn facilities, as well as commercial incineration facilities.

- *Technology Advantages over Baseline*

At present, there is no baseline technology for continuous monitoring of toxic metals. Emissions monitoring is currently performed using extractive sampling and laboratory analysis in accordance with US EPA reference methods. Such tests are time-consuming and costly, approaching $50,000 per week for comprehensive multipoint emissions testing. Furthermore, standard procedures for waste treatment facilities involve characterization of all waste feeds, known as front-end waste characterization. This procedure is costly, time-consuming, and exposes facility personnel to toxic wastes. Implementation of *in situ*, real-time stack monitoring addresses all of these issues, producing cost savings, providing regulatory assurance, and reducing worker exposure to hazardous wastes.

Competing technologies being developed for continuous monitoring of metal emission include inductively-coupled plasma (ICP) atomic emission spectroscopy and X-ray fluorescence spectroscopy. A prototype ICP system has been developed by the United States Navy that makes use of an extractive sampling probe followed by on-line ICP analysis (Seltzer, 2000). A gas sampling interface provides continuous sampling followed by analysis once every 60 seconds. X-ray fluorescence systems typically employ continuous gas sampling and filtration to concentrate metal species, followed by periodic X-ray analysis (Cooper, et al. 2000).

Demonstration Summary

- *Demonstration Sites*

This report covers the period from 6/93 through 6/99, and covers technology development and field demonstrations conducted by personnel from Sandia National Laboratories, Livermore, California.

Clemson University Vitrification Test Facility, Clemson, North Carolina (1995). The test was successful in demonstrating field operation of the original prototype instrument, however, the detection of metal emissions at the operating levels of the vitrification facility proved unsuccessful.

Plasma Hearth Facility at the SAIC STAR Center, Idaho Falls, Idaho, and the **U.S. EPA Incineration Research Facility, Jefferson, Arkansas** (1996). An upgraded prototype monitor was fabricated and evaluated. These two field tests provided critical data to as to the relevant conditions for *in situ* detection of metal emissions in actual waste streams, which enabled a critical assessment of the LIBS monitor performance.

Balboa Pacific Corporation, Santa Fe Springs, California (March 1997). Field demonstration at a private pyrolytic waste treatment facility to assess new conditional data processing algorithms. The Clean Air Act metals manganese and chromium were detected at low part per billion concentration levels in excellent agreement with independent monitoring results.

TSCA Incinerator, K-25 Site, Oak Ridge, Tennessee, and the U.S. EPA Rotary Kiln Incinerator Simulator, Research Triangle Park, North Carolina (final quarter of FY97). These tests demonstrated real-time instrument response to targeted metal species. All data analysis and reporting procedures were automated and performed in real-time.

Contained Burn Facility at Naval Air Weapons Station, China Lake, California (Jan. and Feb. 1998). Field trials were performed in coordination with Department of Defense Demilitarization Programs. Tests demonstrated the rapid response and large dynamic range (factor of 1000) for *in situ*, real-time monitoring of lead emissions.

ICI Explosives Environmental, Inc. Incineration Facility, Joplin, Missouri (April 1999). Test at a commercial explosives incinerator with very low emissions demonstrated monitoring at levels well below newly promulgated emissions regulations.

- *Key Results of Field Demonstrations*

The field tests summarized above were successful in demonstrating the LIBS-based monitor as a technically sound approach for continuous monitoring of metal emissions. Notably, the LIBS system was on-line for all field tests, and functioned in an automated, real-time manner. Furthermore, the instrument was configured for *in situ* measurements, requiring no sample probes or sample extraction. Overall, the LIBS-based monitor demonstrated accurate, real-time response to stack emission, large dynamic range (factor of 1000), and response to transient changes as low as several minutes. Detailed test data are presented under the Performance section and in Appendix B; comparison with independent EPA Reference Method emissions data has demonstrated exact agreement at low part per billion (ppb) concentrations during field trials, while differences approaching one order of magnitude were revealed during select test conditions.

- *Regulatory Considerations*

At the time of this report, the US EPA does not require the use of CEM technologies for comprehensive monitoring of toxic metal emissions. However, the EPA is moving forward with regulatory requirements for continuous monitoring of mercury and fine particulate matter (PM), and continues to encourage the development and testing of continuous multi-metals monitors for thermal treatment facilities. Recent regulations promulgated for volatile and semi-volatile toxic metals hazardous waste combustors (e.g. 64 FR 52828) provide the regulatory infrastructure to accommodate multi-metals CEMs as they are developed.

- *Commercial Availability and Technology Readiness*

At the time of this report, no LIBS-based multi-metals CEMs are available commercially, nor is Sandia National Laboratories party to any licensing agreements concerning this specific technology regarding multi-metals CEMS.

- *Future Plans*

Sandia National Laboratories remains committed to the development of the LIBS-based monitoring technology, and continues to improve and evaluate this technology as part of other program areas. There are no immediate plans for long-term deployment of this technology under DOE sponsorship. Nonetheless, all parties remain interested in the LIBS CEM system.

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All published Innovative Technology Summary Reports are available on the OST Web site at www.em.doe.gov/ost under “Publications.” The Technology Management System (TMS), also available through the OST Web site, provides information about OST programs, technologies, and problems. The Tech ID for Metal Emissions Monitor for DOE Mixed Waste Thermal Treatment is AL-33C2-31.

SECTION 2

TECHNOLOGY DESCRIPTION

The primary objectives of this project were to complete the design, engineering and fabrication of a LIBS-based monitor system that can operate continuously and reliably in field environments, notably at waste treatment facilities in the DOE complex. A detailed description of the LIBS-based monitoring system follows.

Overall Process Definition

- *Laser-Plasma Spectroscopy*

Laser-Induced Breakdown Spectroscopy (LIBS) is the analytical technique that is the basis for the developed multi-metals CEM system. LIBS is an atomic emission spectroscopy technique that makes use of the optical emission produced by the laser-induced breakdown or laser-induced plasma phenomenon. A schematic of the current LIBS system is presented below. A high peak power, pulsed laser beam is focused directly into the targeted waste stream to form a small laser-induced breakdown (i.e. laser spark). The plasma forms from the ionization of both gaseous and particulate species in the waste stream due to the intense laser field strength. Once initiated, the plasma heats a volume of gas equal in diameter to about 0.8 mm to temperatures nearing 25,000 K. At this temperature, all molecules and small particles are dissociated into single atoms within the energetic plasma. The electrons within these atoms gain energy, and subsequently emit light at characteristic wavelengths as the plasma cools and the electrons relax to their original condition (i.e. ground state). This process is known as atomic emission, and forms the basis of LIBS as an analytical technique. Both atomic emission bands and continuous broadband emission characterize the plasma emission. The plasma emission can be processed both spectrally and temporally to identify unique atomic emission bands, which like fingerprints, enable the identification of constituent elements within the plasma. Furthermore, the intensity of the recorded atomic emission lines is used to quantify elemental concentrations.

Key Components of LIBS System
Laser: Nd:YAG, 1064 nm wavelength , 375 mJ/pulse, 10 ns pulse width, 5-10 Hz rep. rate
Spectrometer: 0.275-m spectrometer, 2400 gr/mm grating, 0.12-nm optical resolution
Detector: Intensified charge-coupled device (iCCD), 1024x256 pixel array, time-gated
Control: PC-based computer (500 MHz), Windows 98, LabView software

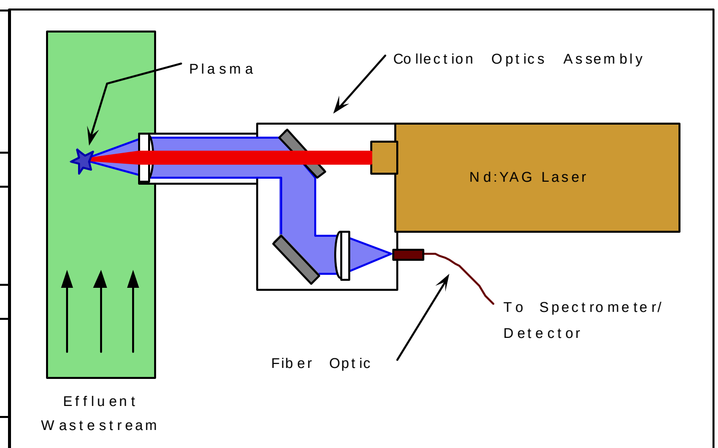


Figure 1. Key components and schematic of LIBS-based emission monitor.

Figure 2. LIBS monitor system installed on Confined Burn Facility, China Lake, California (left), and being installed on the TSCA Incinerator, Oak Ridge, Tennessee (right).

- *LIBS System Specifications*

The current LIBS-based CEM system operates by firing the laser beam directly into the process exhaust stream to create the laser-induced plasma, as depicted in Figure 1. The excitation source for the LIBS system is a 1064-nm Q-switched Nd:YAG laser operating at a wavelength of 1064 nm, with a nominal pulse width of 10 ns, maximum pulse energy of 375 mJ, and with a 5-10 Hz pulse repetition rate. The laser beam is expanded to 12 mm diameter using a 1.5x telescope. The beam expansion aids in the formation of a sharp focal spot for reliable plasma formation. The expanded laser beam is focused into the effluent waste stream using a 75-mm UV grade lens to create the plasma (f/6.25). The plasma emission is collected along the incident beam in a backward direction and separated using a broadband, aluminum coated pierced mirror. The collected plasma emission is then focused onto a UV-grade fiber-optic bundle, and coupled to a 0.275-m spectrometer, dispersed with a 2400-groove/mm grating (0.03 nm/pixel, 0.12-nm resolution), and recorded with an intensified, charge-coupled device (CCD) detector array. In addition, high-resolution spectrometers have been successfully demonstrated on this system to distinguish closely-spaced analyte emission lines, such as the Cd (I) 228.802-nm and As (I) 228.812-nm line pair (Baldwin et al., 2001). The emitted light from the plasma is collected and processed in real-time using a spectrometer and detector system controlled by a single PC or laptop computer. Due to differing rates of decay between the plasma continuum emission (Bremsstrahlung and recombination) and the atomic emission of targeted analytes, temporal gating is necessary for optimal detection. Temporal signal processing is achieved by gating the CCD intensifier, typically using delays from 10 to 40 μs with respect to the plasma-initiating laser pulse, for the targeted metals, primarily the Resource Conservation and Recovery Act (RCRA) metals arsenic, beryllium, cadmium, chromium, lead and mercury. Temporal gating issues are further discussed in the Appendix.

- *LIBS Data Processing*

The original LIBS instrument design utilized a straightforward ensemble-averaging approach for data processing. Specifically, spectra from 100 to 500 laser pulses were collected and averaged to produce a representative spectral signal. Such an averaging technique is useful for eliminating random signal shot-noise. However, detailed calculations demonstrated that for metal concentrations and particle size ranges expected within the normal operating range of effluent streams, the probabilities of sampling toxic metal particles can become limiting (Hahn et al., 1997). The ensemble averaging of metal analyte signals with a low particle sample rate (~1%) can reduce the signal-to-noise ratio to well below the detection threshold (i.e. limit of detection) required for EPA multi-metals compliance monitoring. To avoid these detection limit problems, a technique was developed that enables the separation of laser-induced plasmas that sample a given analyte species (i.e. particle hit) from those laser pulses that sample no metal-containing particles.

A novel approach was developed and implemented for the LIBS-based metals monitor that is based on independent, fixed-rate sampling combined with the conditional analysis of each single laser-induced plasma in an overall sequence of laser pulses. The conditional analysis scheme functions by comparing the intensity of the targeted analyte emission line to adjacent, featureless continuum emission intensity. If the ratio exceeds a set threshold, the spectrum is classified as a hit, and is retained for subsequent data analysis. The LIBS system employs real-time conditional data processing for a total number of laser shots, typically 600 to 1200, after which an average spectrum is generated based on the arithmetic average of the spectra recorded for each identified hit. An equivalent metal concentration is then calculated using a calibration curve, as with any quantitative LIBS analysis. The true or actual metal effluent concentration is then calculated from the product of the equivalent metal concentration (i.e. hits only) and the frequency of particle hits, where the frequency is the number of conditional spectral hits divided by the total number of laser pulses. A schematic of the LIBS data processing scheme is shown in Figure A1 in the Appendix, and complete details of the conditional analysis approach are presented in recent publications (Hahn, et al. 1997; Hahn and Lunden, 2000).

As implemented, the current Sandia LIBS system runs at 10 Hz. This allows 1000-pulse sequences to be completed in less than 2 minutes, which is sufficient for true continuous emissions monitoring. The ratio and conditional analysis threshold may always be selected such that each laser pulse and corresponding spectrum are classified as a hit, in which case the system reverts to a conventional ensemble-averaging system. By running the system at a fixed sampling frequency (i.e. laser pulse rate) of 10 Hz, an independent and random sample selection is realized. This corresponds spatially to samples separated by about 20 cm each for a nominal effluent duct flow of 2 m/s. By sampling at a fixed rate, it is expected that the frequency of hits is representative of the true particle loading for a sufficient number of hits, which is about 20. This eliminates a significant potential source of sample bias that may be introduced by trying to actively trigger the laser based on *a priori* particle detection. In other words, for this technical application any attempt to detect particles in the target volume, for example using laser light scattering, and then initiate a laser spark would be prone to both particle size biases and particle composition biases. An example of the improvements in analyte signal strength with conditional data processing is demonstrated in Figure 3.

- *LIBS Targeted Elements*

The LIBS monitor systems is targeted for the RCRA metals arsenic, beryllium, cadmium, chromium, lead and mercury as present in waste treatment effluent streams. Other Clean Air Metals are accessible with the LIBS technique.

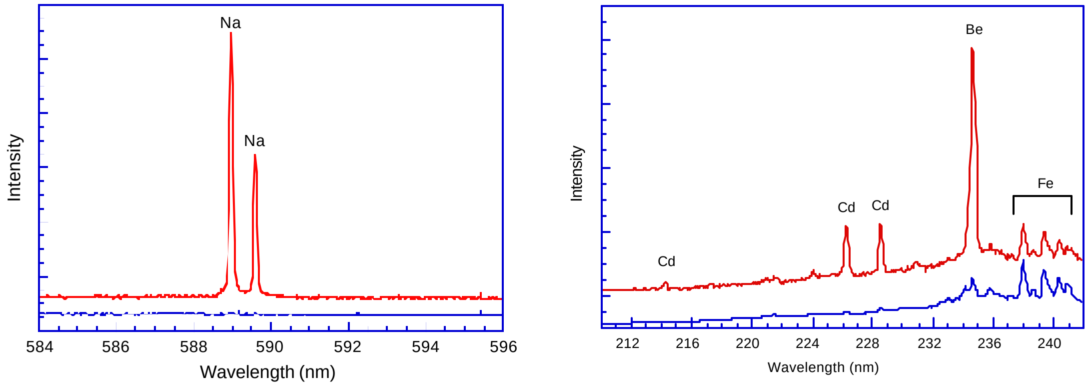


Figure 3. Improvements in analyte signal-to-noise ratios with conditional data analysis. The lower spectrum (blue) represents an ensemble-average of all laser shots, while the upper spectrum (red) represents an average of the spectra identified as containing the analyte signal of interest.

System Operation

The prototype LIBS monitor system is designed for fully automated stack sampling, data analysis, and data reporting. The LIBS system operates in an *in situ*, noninvasive mode, as described above, with remote system operation and control via a remote PC platform coupled to the stack-mounted instrument using a high speed GPIB/IEEE fiber optics communications cable. The LIBS probe mounts directly to the stack via a standard 4 or 6-inch flange, and the probe/stack interface is designed for continuous monitoring with no external cooling requirements. Typically, a low flow rate of dry air or nitrogen (~5 liters per minute) is used to purge the primary focusing optic, which is helpful for prevention of deposits on the lens. External power requirements include a 110 V, 5 amp power supply, and a 220 V, single-phase, 10 amp power supply. The instrument utilizes an internal uninterruptible power supply with voltage regulation and surge/noise suppression. The overall LIBS laser probe module weights about 75 lbs. and has dimensions of approximately 12”x10” in cross-section and 36” in length. The probe module is shown in Figure 2. One supporting instrument rack (30”x30”x48”) is stationed within 12 ft. of the laser probe module.

Two persons of average technical competence can install the overall LIBS system in a time period ranging from 1 to 6 hours, depending on the accessibility to the effluent stack. It is noted that the installation at the TSCA Incinerator, which was within a radiological control area, was completed in less than one 8-hour day. Once installed, a single person can operate the LIBS system with minimal training. The prototype software allows for fully automated emissions monitoring and data logging. With the current system, the operator must start and stop the laser system, remove and insert the probe module, and administer the monitoring scripts for the detection of desired analytes. Full automation, including remote control of the laser, is readily achievable without modest changes to the system software. The LIBS system should be capable of running unattended for 24 hr. periods.

Potential Concerns

For *in situ* stack monitoring, the current prototype LIBS system presents no risks or potential concerns to site personnel. The laser safety is addressed in detail below, but it is noted that the LIBS probe and laser spark are totally enclosed in the effluent stack under operating conditions, thereby posing no threat to site personnel. Interlocks may be readily incorporated into the system for long-term deployments to provide an added measure of safety during laser probe module installation, operation, and service.

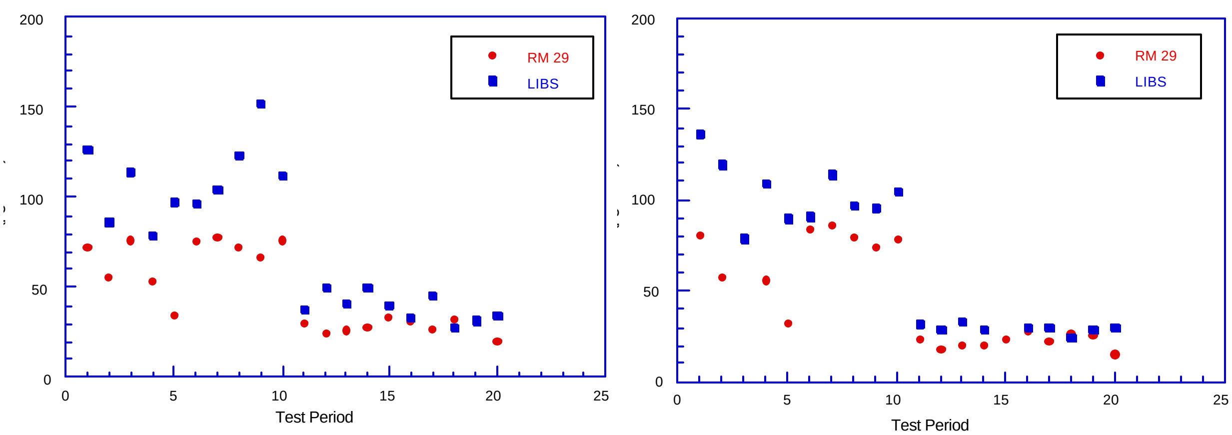
SECTION 3
PERFORMANCE

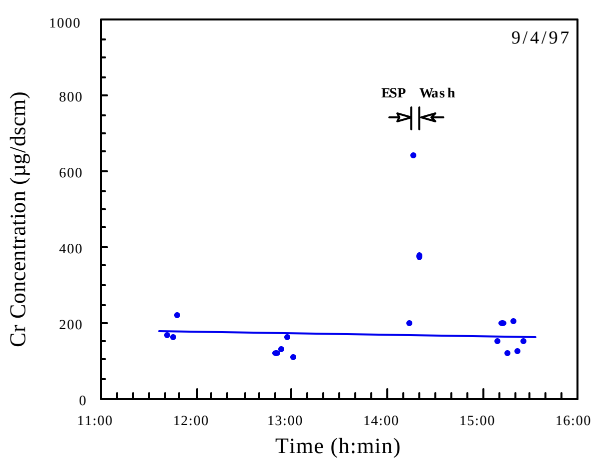
Demonstration Plan

The primary demonstration sites for the prototype LIBS monitor were thermal waste treatment facilities, notably waste treatment sites within the DOE complex. However, due to cost, scheduling, and availability considerations, several field demonstrations were performed at non-DOE sites. For all field tests, the major objective was to assess the response of the LIBS monitor to targeted metal species. Of principal concern were the instrument accuracy, precision, response time, on-line availability, and reliability. When possible, independent reference measurements (extractive sampling) were recorded in accordance with US EPA Reference Methods. Complete LIBS sampling data along with EPA Reference Method extractive sampling data are included in the Appendix. All field tests were designed to assess the overall utility of the real-time emissions monitor, including assessment of the impact on facility operations. However, no detailed cost analyses (e.g. cost/benefit) were performed for the relatively short field demonstrations, which were all less than one week in duration.

Results

i) TSCA Incinerator and EPA Rotary Kiln Incinerator Tests (August/September 1997)





Figure(s) 4. Comparisons of real-time LIBS data with extractive Reference Method data (RM 29) at the Rotary Kiln Incinerator Simulator field test during September 1997 (upper two). Transient changes detected in chromium emissions with the LIBS monitor at the TSCA Incinerator during a 4-min. wash cycle of the electrostatic precipitator (ESP Wash).

The Sandia metal emissions monitor system was evaluated at two sequential field tests during the final quarter of FY97. The first test was at the DOE TSCA Incinerator, K-25 Site, in Oak Ridge, Tennessee, and the second test was at the U.S. EPA Rotary Kiln Incinerator Simulator (RKIS) facility in Research Triangle Park, North Carolina. The TSCA Incinerator test was significant because the facility is a full-scale production unit that treats toxic and low-level radioactive waste (mixed waste) from the DOE complex in Oak Ridge. The LIBS monitor was installed in a radiological control area and operated remotely from a control room outside of the radiological control area. The RKIS test facilities provided a well-controlled range of metal concentrations for evaluation of several metal emission monitor systems under development during a series of blind tests.

The primary goals of these two tests were to (a) demonstrate real-time instrument response to targeted metal species, and (b) to generate real-time data for comparison with independent Reference Method data. The field tests do not reflect more recent additional research focused on optimization of the LIBS system, including temporal signal processing and detailed analysis of gas stream matrix effects on plasma response to targeted metals.

The overall accuracy of the LIBS monitor system varied during these two field tests. As observed in Figure 4, the instrument demonstrated excellent response to changes in metals concentrations, including transient changes as short as 4 minutes in duration. Test results include the quantitative measurement of the RCRA-listed metals beryllium, cadmium, chromium, lead, and mercury, as well as the metals manganese and iron, and yttrium. The LIBS-based emissions data ranged from within 7% agreement with Reference Method (RM) data to about a factor of 8 times high with respect to RM data. Overall accuracy was hindered by several key factors during these two tests, including (a) the failure of a trigger circuit element that shifted the detector temporal gating from the pre-test optimal calibration values, (b) calibration errors due to calibration curve errors at low signal levels realized with ensemble-averaging, (c) non-optimal temporal integration for several species (as discussed in Appendix B), and (d) stack gas matrix effects for several species, notably mercury. Although subsequent research and field tests addressed these issues, these field trials remain important milestones in the critical characterization and assessment of instrument performance under actual waste stream conditions.

ii) Total Containment Vessel Tests (January/February 1998)

Temporal optimization studies were performed following the FY97 field tests to improve the LIBS response to select metals. Significant improvements were made in the detection of chromium and lead using alternative atomic emission lines (405.8 nm for lead, and 426.4 nm for chromium), and significant increases in detector integration delay times, defined as the starting time for plasma emission signal recording with respect to the firing of the laser pulse. As discussed above in the presentation of the theoretical basis of LIBS, the plasma continuum emission and atomic emission decay at different rates, therefore, optimal temporal windows for signal integration (see Appendix) exist that maximize the atomic emission of each analyte with respect to the background emission signal (i.e. signal to noise ratio). An opportunity for a field demonstration using these new optimal detection strategies was presented at the Contained Burn Facility at the Naval Air Weapons Station, China Lake, California in coordination with Department of Defense sponsored Demilitarization Programs through Sandia. The LIBS monitor was deployed to measure lead emissions during a contained burn of Shillelagh anti-tank missiles, which contain 32 grams of lead in the solid propellant. The LIBS system was mounted on a 10-inch transfer duct between the plume containment vessel and the entrance of a HEPA filtration system. The field tests were conducted to demonstrate the rapid response and large dynamic range (factor of 1000) for *in situ*, real-time monitoring of lead emissions.

The LIBS system measured lead using the 405.8-nm emission line, a delay following the laser pulse of 50 μs, and an integration gate of 100 μs. Figure 5 shows the LIBS-based measured lead concentrations during four individual Shillelagh rocket motor burns spaced over a period of a month. These data were taken with one data point every 30 seconds, corresponding to an ensemble average of 150 laser shots, and all data were recorded and processed in real-time using remote operation of the LIBS system. The data in Figure 4 demonstrate the ability of the *in situ* Sandia LIBS monitor to a) respond rapidly to changes in concentration, b) work over wide ranges in concentration, and c) operate in high concentrations and low concentrations without residual signal from the high concentration measurements. The Pb measurement in the transfer line spanned approximately three orders of magnitude in signal, from 50 μg/acm to 50,000 μg/acm. The rapid rise in signal was captured very well by the real-time data from the LIBS instrument. The instrument had the dynamic range to capture all of the pertinent data from this test, and unlike extractive methods, the LIBS instrument was not fouled by the high concentrations. Other candidate CEM methods have reported being unable to use their instruments following a high concentration spike of Hg or Pb, until their extractive probes were cleaned. The *in situ* LIBS instrument, however, does not have a problem with a wide range of metal concentrations, and yielded consistent data over a period of a month. In addition, time-integrated LIBS measurements agreed very well with time-averaged extractive sampling techniques.

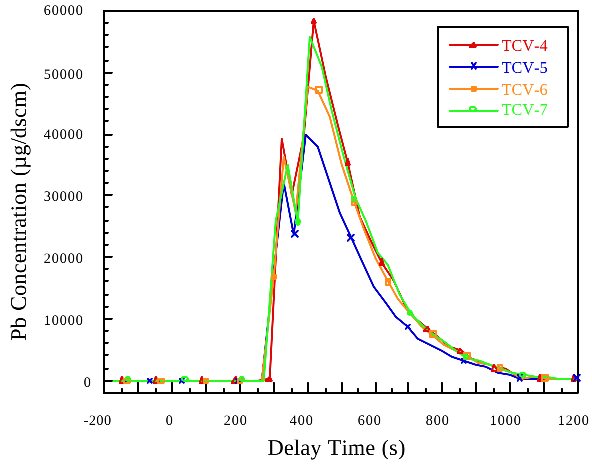


Figure 5. Transient lead emissions as measured with the LIBS monitor at the Contained Burn Facility following a Shillelagh rocket motor burn.

iii) ICI Environmental Explosives Incineration Facility (Spring 1999)

The ICI Environmental Explosives Incinerator in Joplin, Missouri, was the site of a field trial in April 1999. This facility is permitted to destroy a wide range of explosives and primers containing Pb, Cd, Cr, Ba, and other elements. One feature of the incinerator is that the Gore-Tex™ baghouse filters used result in extremely low particulate emissions. During the test burn, waste feeds consisted primarily of fired primers containing high levels of Pb, which translated into an average concentration of approximately 30 micrograms per dry standard cubic meter. Figure 6 shows the measurement of Pb at two-minute intervals during the test burn. The LIBS-based measurements were successfully recorded at concentration levels well below the semi-volatile metals limits for both current and new incinerator sources (240 and 24 µg / dscm), as discussed in Section 7, below.

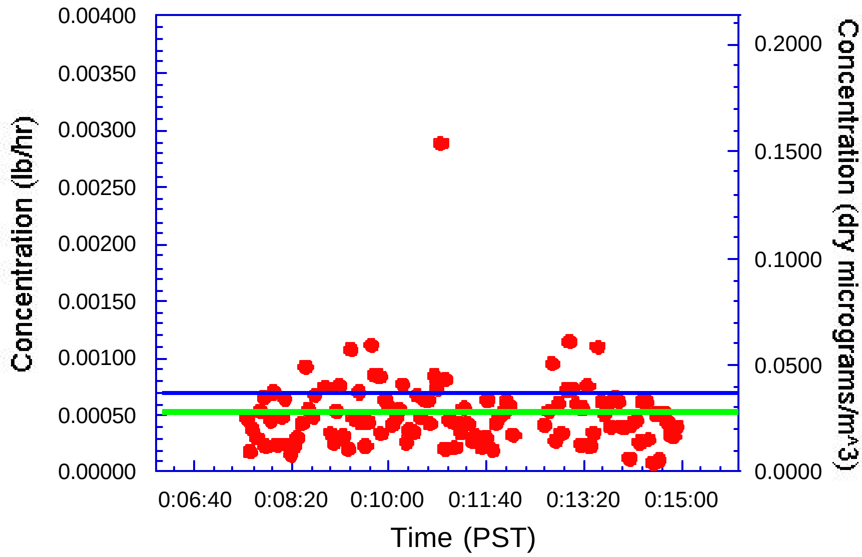


Figure 6. Continuous Pb emissions measured at 2-minute intervals during explosive primer destruction at the ICI Explosives Incinerator. (Green line is LIBS average, blue line is previous (1995) reference method average under identical conditions)

- *Field Demonstration Summary of Results*

Overall, the Sandia LIBS instrument performed reliably over all field tests. The tests all functioned to provide data for the critical assessment of instrument performance and accuracy throughout the development process. The field tests were successful in demonstrating: (i) real-time response to targeted metal species, (ii) fully automated on-line data processing analysis, and (iii) 100% on-line reliability of all test periods. Overall, consistent stack concentration readings were recorded with the LIBS monitor, in good agreement with independent Method 29 reference data. Complete LIBS and RM data are presented in Appendix B. The conditional data analysis approach was very useful in increasing the LIBS sensitivity through discrete particle detection, yielding signals with significantly enhanced signal-to-noise ratios as compared to conventional ensemble averaging. The Sandia monitor also accurately tracked transient changes in metals feed rates and enabled detection of transient increases in metals emissions unavailable with conventional extractive sampling techniques. Overall, the four field tests summarized above demonstrate that a LIBS-based continuous emissions monitor for metals can provide real-time response and concentration measurements in a variety of pilot-scale and production scale waste treatment facilities.

- *Assessment of Instrument Sensitivity and Detection Limits*

The LIBS instrument is designed as a continuous multi-metals emissions monitor, primarily for detection of the RCRA metals arsenic, beryllium, cadmium, chromium, lead, and mercury from the effluent streams from thermal waste treatment facilities. For implementation, the LIBS detection limits must be compatible with typical metals concentration levels in effluent streams, which can be evaluated in terms of the regulatory standards. The new US EPA Maximum Achievable Control Technology (MACT) standards discussed and referenced in Section 7 for emissions from existing hazardous waste incinerators serves as a baseline for emissions levels. The MACT standards are defined for groups of metals, with current emission limits defined as follows: (i) the semi-volatile metals (Pb and Cd) limit is 240 micrograms per dry standard cubic meter (μg/dscm) for total lead and cadmium, (ii) 130 μg/dscm for mercury, and (iii) the low-volatility metals (As, Be and Cr) limit is 97 μg/dscm for total arsenic, beryllium and chromium. For new incinerators, the MACT emission standards are reduced to 24 and 45 μg/dscm for the total semi-volatile metals and mercury, respectively. Assuming equal distributions of metals within each group, and using the new MACT standards, upper limits for metals emissions range from 12 to 45 μg/dscm for these six metals. The MACT standards are somewhat different for new cement kilns, with limits of 54, 56, and 180 for the low-volatility, mercury, and semi-volatile metals, respectively.

For comparison purposes, LIBS based detection limits are summarized in Table I. However, due to the unique sampling nature of LIBS, including conditional analysis, it is difficult to define detection limits. As such, several methods were used to establish the data presented below. Specifically, detection limits are (i) based on traditional ensemble-averaging of multiple LIBS spectra making use of the optimal temporal gates (Ensemble Average), (ii) based on conditional analysis utilizing detection of single particles corresponding to the minimum detectable mass and fifteen minute sample period (Conditional - Min), and (iii) based on conditional analysis utilizing detection of single particles corresponding to 1 micron in size and a fifteen minute sample period (Conditional – 1 μm). Overall, for metals existing as particulates, or absorbed onto other particles such as fly ash, LIBS-based monitoring with conditional data analysis is characterized by detection limits that are compatible with the detection of RCRA metals at concentration levels consistent with new, more stringent MACT emissions standards.

Table I. New MACT emissions standards for the RCRA metals and LIBS-based minimum detection limits for ensemble-averaging and conditional data analysis sampling modes.

Element and Emission line	MACT Standard	LIBS (Ensemble-Average)	LIBS (Conditional - Min.)	LIBS (Conditional - 1μm)
As (228.8 nm)	32 μg/m^3	400 μg/m^3	0.8 μg/m^3	7 μg/m^3
Be (313.1 nm)	32	10	0.02	4
Cd (226.5 nm)	12	60	0.1	16
Cr (425.4 nm)	32	30	0.1	13
Hg (253.7 nm)	43	230	0.5	11

Pb (405.8 nm)	12	190	0.4	20

SECTION 4
TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

- Current methodology – Strengths and weaknesses

The EPA currently mandates the use of Reference Method 29, Multi-Metals from stationary sources. This has been referred to as the Reference Method (RM) earlier in this document. This test involves isokinetic extraction of stack gas over the period of approximately 1 hour, through a heated filter and an impinger train with specified strong acid solutions for capture of the metal species. The probe is traversed radially, most properly in two orthogonal directions (depending on the size and geometry of the stack) to obtain a representative sample. The volume and temperature of the stack gas sampled is carefully measured, and all sample lines and glassware are carefully acid washed following each run. The filter catch, impinger solutions, and the wash are all analyzed for metals in an analytical laboratory, typically using ICP-MS, atomic absorption spectroscopy, or other technique for elemental analysis.

The strength of Method 29 is that it has been well-proven in a variety of situations. While the methodology is not perfect (for example some elements such as Sb oxides are suspected to be not well-digested by the acid solutions specified in the method) [Cooper, 2000], the method is relatively robust and well known to practitioners. However, the method is also extremely slow and expensive, providing data in a matter of weeks and at an approximate cost of $5000 per one-hour test. Hence this method is able to simply provide a snapshot of emissions at a particular time. It is the backdrop of Method 29 that has spurred the development of alternative technologies. Note that Method 29 is not considered a true “baseline” method for across-the-board comparison on matters other than time-averaged concentration with LIBS and other multimetals CEM technologies, as the reference method is not a CEM technology.

- Criteria for acceptance of alternative methods

The U.S. EPA has published suggested guidelines for acceptance of multi-metals CEM methods, in Performance Specification 10 (Emissions Measurement Center, 1997). These suggested guidelines outline the following: (1) Procedure and time for calibration, span, and drift checking, (2) Response time, (3) Measurement locations, and (4) Comparison with Reference Method 29. In brief, the two most important criteria are that the multi-metals CEM have a relative accuracy (as defined in PS-10) within 20% with respect to the Reference Method, and that the CEM be able to make a stable measurement in less than 2 minutes, unless no other existing CEM can make the measurement within that time.

- Alternative technologies – strengths and weaknesses

i) Argon Inductively Coupled Plasma

One of the more developed of the alternative multi-metal CEM technologies, an argon inductively-coupled plasma (ICP) CEM has been demonstrated by Dr. Mike Seltzer and co-workers (Seltzer and Meyer, 1997; Seltzer, 2000) from the Naval Air Warfare Center, China Lake, California, and is under commercialization by Thermo Jarrell Ash Corporation. In this system, gases are sampled continuously through a specially designed nozzle that minimizes aerosol sample deposition (Fan, 1992) and passed through a heated transfer line into a sample loop from which they may be subsequently drawn in to the ICP or bypassed to exit the unit. Prior to use of the shrouded nozzle assembly and a shortening of the transfer line, tests had indicated significant deposition in the nozzle and transfer line. The latest paper (Seltzer. 2000) indicates that deposition continues to be sensitive to the orientation and the length of the transfer line. After a significant (i.e. many months) amount of work on-site at installations at WTI and an APE 1236 munitions deactivation furnace (Toelle Army Depot), the developers have demonstrated results within the EPA relative accuracy requirement for Ba, Cr, Mn, Ni, Pb, Sr, and Y, including data from selected test runs, varying from 3-9 out of the total 12 runs (Seltzer, 2001). In addition, Cd and Co were very close (20.4% relative accuracy) to the suggested 20% relative accuracy.

Detection limits for argon-ICP systems are generally about 1-2 orders of magnitude better than LIBS ensemble-averaged detection limits, due to the higher duty cycle of the process, and on par with LIBS conditionally-averaged detection limits. However, analysis of single particles is not possible with an argon-ICP system. As noted in the recent paper [Seltzer, 2000], "careful optimization of the sampling process, with particular attention paid to minimizing sample aerosol deposition losses" is required to achieve results consistent with the reference method. This method, then, requires significant attention by trained scientists to make accurate measurements at each measurement site. It is not known how much continuing operator attention is required. In addition, due to the size of the analytical system and associated hardware, the argon-ICP system as fielded has been contained in a relatively large shelter located very close to the sampling site to minimize aerosol deposition losses, which may be prohibitive for some applications. These concerns aside, this method is among the first of the multi-metals CEM techniques to meet the relative accuracy requirement for some toxic metals. Its proponents have worked diligently to make this technique successful, and have integrated their efforts with a commercial manufacturer to make this technology available in the marketplace.

ii) Air Inductively Coupled Plasma

Researchers at Mississippi State University Diagnostic Instrumentation and Analysis Laboratory (DIAL) have been working on an air-ICP system, similar to the argon-ICP system described above. This system was tested in 1997 at the U.S. EPA rotary kiln incinerator. Recent developments have included coupling the plasma system with an echelle spectrometer for greater wavelength resolution (Baldwin et al., 1999).

iii) Microwave Plasma

Also similar to the argon-ICP system described above, a microwave plasma system is under development by researchers at the Massachusetts Institute of Technology. First described in 1996 (Woskov et al., 1996), the microwave inductively-coupled plasma has the advantage that it is more robust than an air or argon plasma, and can directly accept a large undiluted exhaust flow. Another benefit to this technology is that it uses inexpensive mass-produced kitchen microwave sources. This work has emphasized *in situ* plasma generation (in the stack) and the developers have also worked out a method for *in situ* span and calibration. This method has met the relative accuracy requirement for Be and Pb, but has detection limits for these metals of on the order of mg / m^3, as opposed to the µg / m^3 that will be required to meet upcoming regulations. If the detection limits can be improved substantially, the fact that this method does not rely on extractive sampling could be a significant advantage for metals monitoring using this technology.

iv) X-ray fluorescence

An X-ray fluorescence (XRF) CEM is under development by John Cooper and colleagues at Cooper Environmental Services (Cooper et al., 2000). In this system, an isokinetic stack sample is drawn through a 1-inch stainless steel transfer line and into a stilling chamber to reduce the velocity. From this chamber a second sample is drawn isokinetically, diluted by nitrogen, and directed through a filter that captures both particulate and ionic gas-phase species. The entire sampling apparatus is kept at elevated temperatures similar to stack temperatures (here 350 °F). The filter is on a tape that can advance automatically. Every 11.5 minutes the tape advances and an energy dispersive X-ray fluorescence analyzer determines the elemental mass in the collected sample. In a recent test at a plasma arc treatment facility, this system met the 20% relative accuracy requirement for both lead and chromium. The primary disadvantages to this method include the long time required for sufficient sample collection to perform the XRF analysis, and the uncertainties associated with extractive sampling.

Technology Applicability

The LIBS technology is one of several emerging technologies designed to fill a need in multi-metals continuous emissions monitoring. This technology is applicable to measurement of emissions from any process stream emitting metals in either particulate or vapor form. Repeated measurements in the laboratory have shown that the LIBS technique has equal sensitivity to either particulate or gas phase atoms. The primary characteristics and differentiators of LIBS measurements with respect to other measurement techniques include 1) the real-time nature of the measurement, and 2) the *in situ* nature of the measurement. The first characteristic makes the measurement amenable to feedback / process control applications, and the second characteristic eliminates the potential bias that may be caused by extractive sampling. Other CEM methods have encountered difficulty with deposition in extractive sampling lines and resulting bias, and typically sample over a relatively long period, making the measurements unsuitable for feedback control applications.

Patents/Commercialization/Sponsor

Numerous patents exist for LIBS technology. The primary patent that is important for LIBS-based multimetal CEMs is U.S. Patent #6,061,641, by David Hahn et al., which is held by Sandia National Laboratories. This patent, granted on May 9, 2000, covers the conditional analysis technique that is described in Section 2 of this report, as well as in Appendix B.

No companies have emerged with a commercial multimetals CEM based on LIBS, although as of the writing of this report, several companies are known to be interested in the concept.

SECTION 5
COST

Methodology

In the absence of baseline CEM technologies and with essentially all competing multi-metals CEM technologies still in development, this section will delineate estimated costs for a commercially available LIBS system.

Cost Analysis

- Fundamental Assumptions

Technology: To meet multi-metal CEM needs requires a sensitive detection system such as the system currently employed by Sandia National Laboratories. The basic system would thus be comprised of a Nd:YAG laser, a spectrometer, a gated, intensified CCD camera, optical delivery system, computer hardware, and integration / packaging hardware. (see Figure 1)

Business: The technology development and integration company will have substantial costs in assembly, application software development, testing, service, and liability for their product. As a result, measurement instruments typically have a sales price of 3-4 times their associated hardware costs. A conservative sales price estimate of 3.5 times the hardware cost will be used in this analysis.

Service: This analysis will assume that a fielded unit requires 6 hours of service every 3 months, plus one yearly trouble visit. In addition, the working life of the instrument in continuous use in the field will be assumed to be 5 years, and 20% of the hardware cost will be set aside each year to cover the cost of replacement parts. This straight-line depreciation assumption is conservative, as in reality the probability of component failures will increase with time.

- Purchase Costs

As indicated above, the basic hardware costs will be multiplied by a factor of 3.5 to obtain the estimated purchase cost of the instrument. Approximate hardware costs are shown in Table II. With these estimated hardware costs, the estimated purchase price of the instrument would be $315,000.

Table II: Estimated hardware costs for LIBS CEM.

Hardware Item	**Estimated cost**
Nd:YAG laser	$25,000
Coupled spectrometer / ICCD camera	$50,000
Optics, probe	$7,000
Computer hardware	$3,000
Integration hardware, casing	$5,000
Total estimated hardware cost	**$90,000**

- Ongoing Costs

Each service call would include time and travel for the manufacturing company's representative to visit the industrial site, for instance to install and/or maintain the instrument, including QA/QC, etc. Assuming that the total of the time and travel for each service call and/or trouble visit is $2,500, then the total yearly budget for service would be $10,000. Assuming that 20% of the hardware cost is set aside to cover replacement parts and refurbishment, this would amount to $18,000 per year. Hence the total ongoing operating costs of the instrument are estimated to be $28,000 per year.

Cost Conclusions

Based on the above, the total cost for the first year (purchase and ongoing operating costs) would be $343,000, and ongoing costs in subsequent years would be $28,000 per year. Total costs averaged over 5 years would amount to $91,000 per year. Currently the majority of large hazardous waste incinerators, boilers, and industrial furnaces are limited in their waste processing capacity either by conservative emissions factors (http://www.epa.gov/oar/oaqps/efactors.html) coupled with detailed waste analysis, or by trial burns with reference methods to obtain more realistic emissions factors coupled with detailed waste analysis. Both the reference methods and the waste analyses are expensive, and either scenario typically leaves the waste process facility operating significantly under capacity. These costs could be offset by a multi-metals CEM, which would obviate the need for both expensive waste analysis and conservative emissions factors, allowing facilities to operate much more closely to their actual permitted limits while remaining within the safe emission limits mandated by the regulatory agencies. This increased throughput available with a multi-metals CEM would increase revenue, while the presence of the CEM would assure communities that safe emission limits are being observed continuously.

As an alternative method of comparison, it is notable that each run of Reference Method 29 costs between $2,500 and $7,500, depending on the conditions, the vendor, and the types of analyses required. State regulations vary as to the frequency of required metals emission measurements for permit certification and compliance; a typical minimum scenario might be a set of 20 duplicate Reference Method 29 challenge runs at 5-year intervals. With a median cost of $5,000 per run, this minimum scenario would amount to analysis costs of $200,000 total. These challenge runs are used to determine emission factors for particular metals, and subsequent to the challenge runs the operator is required to extensively analyze their waste, as discussed above. The reference method and waste analysis costs coupled with lost throughput could easily exceed the yearly cost of a LIBS-based CEM.

SECTION 6
OCCUPATIONAL SAFETY AND HEALTH

Required Safety and Health Measures

The current LIBS monitoring technology presents no significant health or safety risks to process operators or maintenance workers. The only potential hazard is the use of a Class IV laser beam, which can cause tissue or eye damage due to direct beam exposure. However, the current application of emissions monitoring involves *in situ* measurements made directly in an effluent stack, hence the laser beam is completely enclosed. Furthermore, the system design makes use of a sharp focal length lens (75 mm), which causes the laser beam to rapidly expand after the plasma spot and greatly reduces the potential for injury. Engineering controls are readily implemented, including the use of interlocks to shut down the laser if the probe is removed from the stack or if adjacent stack access ports are opened. It is noted that the LIBS-based system does not use ionizing radiation.

Safety and Health Lessons Learned from Demonstrations

There were no safety and health lessons learned from the demonstrations of the technology. Adequate safety training was received by the researchers prior to the demonstrations, and good safety and health practices were consistently followed throughout the field trials. The TSCA Incinerator field trial involved installation of the LIBS system within a radiological control area (RCA). Personnel were required to wear protective clothing, including boots, full body suits, gloves, and hoods within the RCA. Such restrictions did not hinder the successful installation of the LIBS system, and no radiological contamination to personnel or to the LIBS equipment occurred.

Comparison with Baseline and Alternative Technologies

The use of LIBS-based continuous emissions monitoring technologies has two potential benefits concerning the occupational health and safety of workers at thermal waste treatment facilities. First, the use of continuous monitoring technologies ensures that facility emissions levels remain in compliance with permitted emissions limits at all times. While modern waste treatment facilities use a wide range of control technologies, actual emissions levels are highly dependent on the composition of the waste feed stream. Therefore, high emissions may be realized through highly concentrated feed-stocks while overall process controls indicate normal operation. The second potential benefit involves the current standard of front-end waste characterization, where all waste feed streams are sampled for laboratory analysis. A fundamental change from front-end waste characterization to continuous stack monitoring may limit operator exposure to toxic waste streams during the current sample collection, handling, analysis and disposal procedures.

SECTION 7
REGULATORY AND POLICY ISSUES

Regulatory Considerations

LIBS technology is related to compliance process control for hazardous waste thermal treatment units processing waste containing hazardous metals. 40 CFR Part 60 et al. were supplemented in the Federal Register Vol. 64 No. 189, pp 52828 ff. with the promulgation on September 30, 1999, of “NESHAPS: Final Standards for Hazardous Air Pollutants for Hazardous Waste Combustors.” This regulation, which affects hazardous waste incinerators, hazardous waste burning cement kilns, and hazardous waste burning light aggregate kilns, sets new emissions standards for seven of the toxic metals listed on the EPA Air Toxics list. The five metals not listed, nickel, antimony, cobalt, manganese, and selenium, were not listed either because of a paucity of emissions data, low toxicity (antimony, cobalt, and selenium) or because the metals track well with total particulate matter and so the particulate matter standard (57 µg / dscm) provides a good surrogate. Table 3 shows the limits for regulated toxic metals in incinerators:

Table 3: Limits for regulated toxic metals and particulate matter for hazardous waste incinerators.

	Existing sources	**New Sources**
Low volatility metals (Cd, Be, As)	97 µg/ dscm	97 µg/ dscm
Semi-volatile metals (Pb, Cr)	240 µg/ dscm	24 µg/ dscm
Mercury	130 µg/ dscm	45 µg/ dscm
Particulate Matter	34 mg/ dscm	34 mg/ dscm

The promulgated regulations do not require particulate matter, mercury, or multimetal CEMS, citing the EPA judgment that none were reliable enough at the time that the regulation was promulgated to meet the standards of accuracy required for CEMS. Nevertheless, the regulation does extensively discuss both the advantages and desirability of CEMS, and leaves room for future rulemaking addressing specific CEMS pertinent to hazardous waste incinerators. In addition, the promulgated rules do leave open the possibility for implementation of CEMS as they are available on an experimental basis, reducing the reliance on trial burns and emission factors.

Risks, Benefits, Environmental and Community Issues

An important linkage exists between regulations and the availability of CEMS. To some extent, commercial investment and industrial interest in multi-metals CEMS is driven by the requirements promulgated by the U.S. EPA and other regulatory agencies. The fact that the recent regulations have opened the door to allow some reliance on CEMS as they are developed is an important step. Coupled with the fact the CEMS may be able to generate increased revenue for a facility (see **Cost**, above), as well as savings in feed stream analysis, this may be sufficient to open a market for commercial investment in LIBS and other multi-metal CEM technologies, benefiting from significant government investment in these technologies.

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) criteria do not apply to this technology, as it is not associated with a Superfund cleanup. Further, the nine criteria have no relevance to this technology, as the criteria were meant to assess cleanup and remediation methods, rather than diagnostic and measurement technologies. Hence no further discussion of CERCLA is warranted here.

SECTION 8
LESSONS LEARNED

Implementation Considerations

The field tests of the LIBS-based continuous metal emissions monitor at the various facilities were instrumental in demonstrating a real-time response to targeted metal species, as well as providing critical assessments of overall system accuracy and precision under actual waste stream conditions through comparison with the Reference Method 29. Several key items were evaluated during the field tests, notably the ability of the LIBS instrument to perform satisfactorily, as measured by system response to changing analyte concentrations, precision, and accuracy, in several different waste stream gas matrices, including saturated stack conditions and widely varying analyte concentrations, with a single, absolute calibration approach. The stability with respect to waste stream gas composition of the laser-induced plasma spectroscopy as an analytical technique is a strength of this method. Secondly, the coupling of the inherent point sampling of the LIBS technique with the discrete particle nature of most metallic species within the relatively cool post-process effluent streams proved to be a fundamental step in improving overall system response. It is noted that mercury, with uniquely high volatility among the RCRA metals, may exist as a vapor state, thereby negating enhancements in detection with conditional analysis. Overall, the conditional data analysis approach developed in response to early field trials was very useful in increasing the LIBS sensitivity through discrete particle detection. The conditional analysis approach was successful in detecting single particulates under normal operating conditions, yielding signals with significantly enhanced signal-to-noise ratios as compared to conventional ensemble averaging.

In general, an important conclusion with regard to this development program is the need for short field trials at relatively early stages in the instrument development. These initial trials should not be high-profile technology demonstrations, but rather data gathering experiments to provide critical feedback. Such field tests need not be conducted at the sponsor's facilities; hence cooperative facilities should be sought in close proximity to the developers to facilitate ease of testing and to minimize program costs.

Technology Limitations and Needs for Future Development

In contrast to early instrument development, capstone technology demonstrations and assessments should be planned and budgeted for longer duration. The one-week timeframes of the TSCA Incinerator, EPA RKIS, and ICI Explosives Incinerator were not optimal for true critical evaluations. One must keep in mind that such demonstrations are still focused on technologies under development, with instrument systems not to the point of "turn-key" operation. A better assessment of the technology would be possible with tests of two to four weeks in duration, possibly with two Reference Methods performed such that quantitative feedback is provided during the field test. While field tests represent a significant cost item, instrument shipping and installation, as well as participant travel are fixed costs, hence extensions of field trials for several weeks provides only an incremental cost.

Technology Selection Considerations

Traditionally, it is thought that the commercial need for a LIBS-based multi-metals emissions monitor is driven primarily by air quality regulations. While this is largely true, we have found that there is also a substantial advantage to some facilities that could be derived through increased potential throughput and decreased cost associated with input stream monitoring. This need could be a significant driver in the marketplace to improve the LIBS technology. The projected costs annualized over 5 years appear consistent with the resources available to incineration facilities and similar facilities.

In summary, the LIBS instrument described in this report has proven effective and field-worthy in trials at a number of different facilities, with 100% on-line measurements of multiple metals. The fielded LIBS system is able to measure multiple metals at low concentrations; using conditional analysis it is shown that LIBS detection limits are an order of magnitude or more below regulated limits for incinerators for the six primary toxic metals (As, Be, Cd, Cr, Hg, Pb). Results have been shown to be within good general agreement with the EPA reference method, accurately capturing trends (Fig. 3, Fig. 5), and selected metals have been shown to be within the relative accuracy required for CEMs by the EPA. A single, longer-term test is necessary for full relative accuracy requirements to be achieved for a LIBS-based multi-metals emissions monitor.

APPENDIX A
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APPENDIX B
Additional Experimental Details and Data

Conditional Data Analysis

The conditional data analysis routine developed and implemented as part of the LIBS-based emissions monitor is based on the data processing algorithm presented below. Overall, rejecting specific single-shot LIBS spectra that do not contain the analyte signal or signals of interest enhances the analyte sensitivity. Complete details of this data processing routine are presented in Hahn et al. (1997), Hahn and Lunden (2000), and U.S. Patent # 6,061,641.

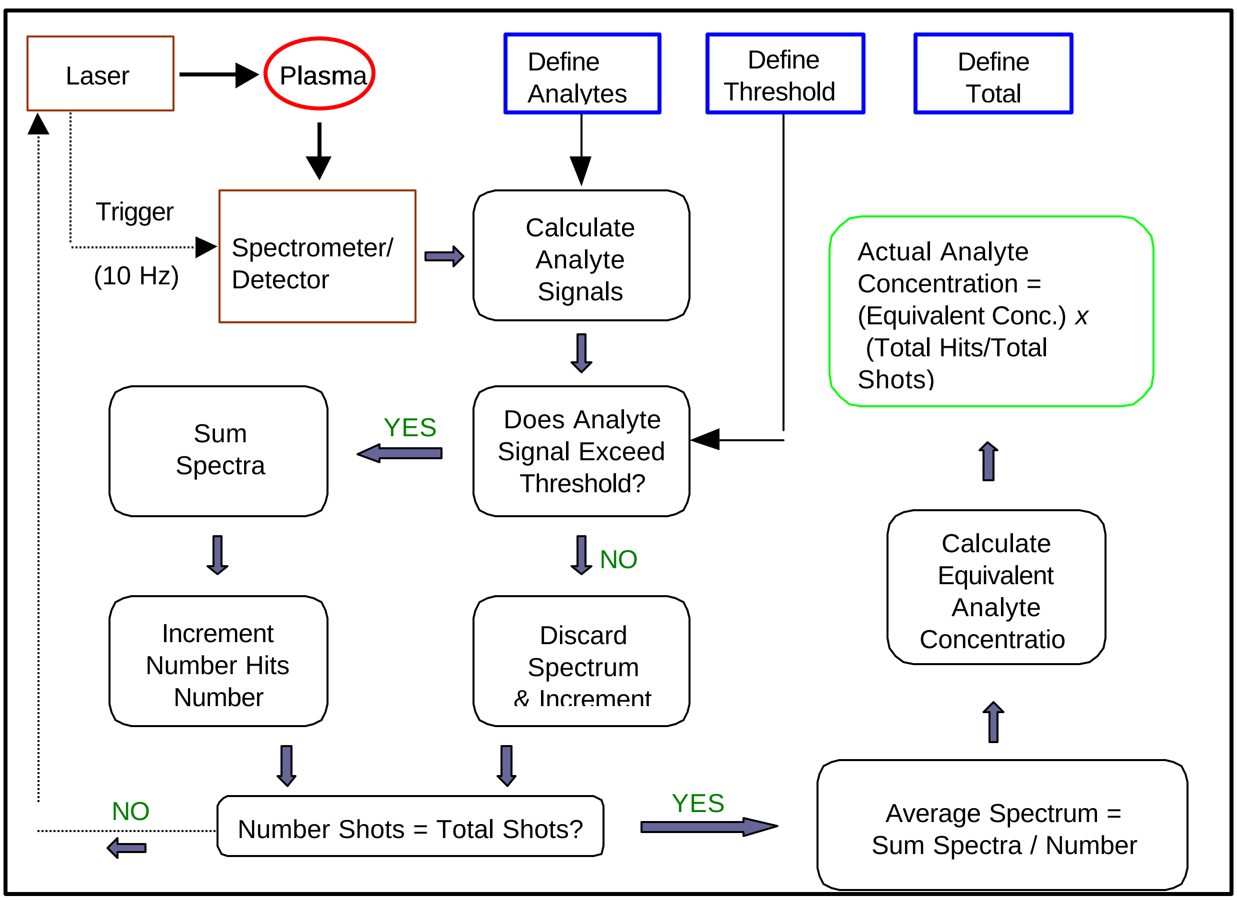

Figure B1. Conditional data processing algorithm for LIBS-based emissions monitor.

LIBS-based Monitor Field Trial Data

i) Balboa-Pacific Pyrolytic Waste Processing Unit
Santa Fe Springs, California
March 1997

Metal	LIBS Measurement (µg/acm)	Reference Method 29 (µg/acm)
Iron	25	40
Manganese	3.3	3.3
Chromium	2.3	2.9
Iron	50	82
Manganese	9.3	4.9
Chromium	1.5	1.9
Iron	91	140
Manganese	7.0	4.5

ii) TSCA Incinerator
K-25 Site, Oak Ridge, Tennessee
August/September 1997

Metal	Low Feed (µg/dscm)		Medium Feed (µg/dscm)		High Feed (µg/dscm)	
	LIBS	RM29	LIBS	RM29	LIBS	RM29
Beryllium	0.04	ND	0.2	ND	0.1	0.6
Cadmium	84	14	87	162	294	896
Chromium	89	11	119	128	182	271
Mercury	200	68	165	110	299	773
Manganese	23	2	17	10	35	26
Lead	57	35	ND	234	95	1124

Relative Accuracy data along with a complete statistical analysis based on EPA performance criteria are presented in Bechtel Jacobs (1998). The range of Relative Accuracy is summarized here.

Metal	%RA
Beryllium	154%
Cadmium	70 to 620%
Chromium	23 to 925%
Mercury	100 to 630%
Manganese	290%
Lead	105 to 375%

iii) EPA Rotary Kiln Incinerator Simulator (RKIS)
Research Triangle Park, North Carolina
September 1997

Metal	Low Feed LIBS (μg/dscm)	Low Feed RM29 (μg/dscm)	High Feed LIBS (μg/dscm)	High Feed RM29 (μg/dscm)
Beryllium	65	20	123	62
Cadmium	29	21	104	69
Chromium	39	27	109	62
Iron	2547	2171	2193	2176
Yttrium	76	182	57	100

Relative Accuracy data along with a complete statistical analysis based on EPA performance criteria are presented in Lemieux et al. (1998). The range of Relative Accuracy is summarized here.

Metal	%RA
Beryllium	175 to 365%
Cadmium	290 to 340%
Chromium	195 to 250%

Calculation of LIBS Detection Limits

Estimated limits of detection for the RCRA metals arsenic, beryllium, cadmium, chromium, lead, and mercury are reported in Table I. The values were calculated based on traditional ensemble-averaging of LIBS spectra, as well as calculated using conditional data analysis based on the minimum detectable analyte mass, or based on a fixed particle size of 1 micron. Details of these three calculations are presented below.

i) *Ensemble-average method*. The detection limit is determined directly from the analyte response function. LIBS data were recorded over a range of known analyte concentrations and a linear calibration curve was constructed. The analyte signal-to-noise ratio (SNR) was calculated as the integrated analyte atomic emission line normalized by the root-mean square fluctuation of the continuum emission in a spectral region adjacent to the analyte emission line. The detection limit is then calculated from the linear response curve for a concentration value that corresponds to a SNR of 3.

ii) *Conditional analysis – Minimum detectable analyte mass* . The detection limit is determined based on conditional data analysis, an approach that is limited by two parameters, namely the minimum detectable analyte mass and the analyte sampling rate. Minimum single-shot detectable particle masses were calculated for each RCRA metal based on each analyte signal-to-noise ratio and corresponding detection limit. In an earlier publication, detailed calculations were presented regarding the minimum number of particle hits (about 20) required for accurate concentration measurements (analyte mass per volume of gas) using conditional analysis. The detection limit is calculated from the product of the minimum particle mass and the particle number density sufficient to sample 20 particles in 15 minutes at a laser repetition rate of 10 Hz, which corresponds to a statistical sample rate of 0.22%. This approach is limited by the minimum detectable analyte mass and the particle sampling rate.

iii) *Conditional analysis – 1 micron sized particle*. The detection limit is determined based on conditional data analysis, as described above, assuming a particle size of 1 micron and relevant particle densities and composition for each targeted metal. The lower detection limit is calculated from the product of the particle mass and the particle number density sufficient to sample 20 particles in 15 minutes at a laser repetition rate of 10 Hz, which corresponds to a statistical sample rate of 0.22%. This approach is limited by the particle sampling rate.

Temporal Signal Optimization

The plasma continuum emission and atomic emission decay at different rates, therefore, optimal temporal windows for signal integration exist that maximize the atomic emission of each analyte with respect to the background emission signal (i.e. signal to noise ratio). Significant improvements in analyte detection limits can be realized by optimizing the detector signal integration gate, defined as the starting time and duration time of plasma emission signal recording with respect to the firing of the laser pulse. Optimal gates for the RCRA metals are summarized below.

Table I. Optimal detector gate (delay from laser/duration of integration).

Element/Line (nm)	Optimal Gate
As 228.81	8 µs / 4 µs
Be 234.86	12 µs / 4 µs
Be 313.1	12 µs / 4 µs
Cd 226.50	8 µs / 4 µs
Cd 228.80	12 µs / 4 µs
Cr 425.44	50 µs / 150 µs
Cr 428.97	50 µs / 150 µs
Hg 253.65	12 µs / 4 µs
Pb 405.78	50 µs / 150 µs

APPENDIX C

ACRONYMS AND ABBREVIATIONS

CEM	Continuous Emissions Monitor
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CIF	Consolidated Incineration Facility
DIAL	Diagnostic Instrumentation and Analysis Laboratory (Mississippi State University)
DoD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
ICCD	Intensified Charge-Coupled Device
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IEEE	Institute of Electrical and Electronics Engineers
LIBS	Laser-Induced Breakdown Spectroscopy
MACT	Maximum Achievable Control Technology
Nd:YAG	Neodymium : Yttrium / Aluminum / Garnet (laser)
OST	Office of Science and Technology
PM	Particulate Matter
RCRA	Resource Conservation and Recovery Act
RKIS	Rotary Kiln Incinerator Simulator
SAIC	Science Applications International Corporation
TMS	Technology Management System
TSCA	Toxic Substances Control Act
US	United States
XRF	X-Ray Fluorescence